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Energy of vacancy formation in silver and aluminium

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Coefficients of thermal expansion of silver and aluminium are determined by X-ray diffraction at different temperatures using a diffractometer, Geiger counter, chart recorder and a specially designed furnace. Equations are given for the variation of lattice constants with temperature. The temperature dependence of the thermal expansion at high temperatures is shown to be related to the concentration of thermally generated vacancies. The energies of vacancy formation in the metals are estimated and found to be in good agreement with other workers. It is also found that the metals obey the 'law of corresponding states'

1. Introduction

The thermal expansion of Ag and Al has been investigated by X-rays by many workers, notably by Esser *et al* (1938), Hume-Rothery & Reynold (1938), Wilson (1942), Ellwood & Silcock (1948), Spreadborough & Christian (1959), and Simmons & Balluffi (1960a, 1960b).

Examining the results on the thermal expansion of the two metals as obtained by different workers, it can be seen from Tables 1 and 2 that they differ much from each other. Such differences are mainly due to the faulty construction of furnaces in which large temperature gradients exist (Williamson & Moore, 1956). A special diffractometer furnace having a large volume of uniform temperature was therefore developed in our laboratory. This furnace and the X-ray technique gave accurate and precise results of the thermal expansion of alkali halides at high temperatures (e.g. Pathak & Vasavada, 1970, hereafter called Paper 1). The reliability of these results could be judged from the fact that they gave correct values of the energy of vacancy formation and a correct relation between the energy of vacancy formation and the melting temperature. It was therefore thought desirable to use the same furnace and to obtain precise data on the thermal expansion of silver and aluminium at different temperatures.

2. Experimental

The experimental observations were taken with the Philips X-ray unit PW 1009 with an external voltage stabilizer, diffractometer, chart recorder and the specially designed furnace. The metal powders were prepared by filing and passing them through 350 and 400 mesh sieves.

Table 1. Coefficient of Linear Expansion α of Ag

Temperature °C	$\alpha(^{\circ}C^{-1}) \times 10^6$ a	b	c	d	Present work
0					18 3
50	19 3				18.8
100	19 7				19 2
150	20.0				19 7
200	20 4		20 3		20 2
250	20 7		20 3	20 8	20.6
300	21 2		20 6	20.5	21 1
350	21 7	21 1	21 0	20 3	21 6
100	22.1	21 5	21 4	20 2	22 1
150	22 5	21 9	21 7	20.2	22 6
500	23 0	22.3	21 7	20 3	23 1
550	23.5	22 7		20.6	23.6
600	24 0	23 2		21 5	24 1
650	24 6	23 7		23 0	24.9
700	25 2	24 3		24 5	25.7
750	25 8	25 0		25 7	26.7
800	26 6	25 7		26 9	27.9
850	27.4	26 5			29 2
900	28 4	27 5			30.7
950	29 4				32 4

(a) Simmons & Balluffi (1960b), (b) Hume-Rothery & Reynolds (1938)
(c) Owen & Roberts (1939), (d) Spreadborough & Christian (1959)

The metal powders were mixed with a small amount of binding material and were annealed in argon atmosphere. The details of the measurements are described in Paper I. The overall accuracy of the results is estimated to be about $\frac{1}{2}\%$ The metals were specpure and obtained from Johnson Mathey and Co., London.

3 Results and Discussion

The lattice constants of the metals were found to vary with temperature according to the following equations The equations were obtained with the help of an IBM 1620 computer

Ag :

From 0 to 550°C

$$a_t = 4{\cdot}0763+7{\cdot}475\times10^{-5}t+1{\cdot}8411\times10^{-8}t^2+2{\cdot}6301\times10^{-12}t^3 \quad \ldots (1)$$

From 500 to 950°C

$$a_t = 4{\cdot}1186+9{\cdot}5513\times10^{-5}(t-500)+1{\cdot}37\times10^{-8}(t-500)^2+4{\cdot}4341\times10^{-11}(t-500)^3 \quad \ldots (2)$$

Al :

From 0 to 350°C

$$a_t = 4{\cdot}0410+9{\cdot}2211\times10^{-5}t+4{\cdot}0505\times10^{-8}t^2-7{\cdot}2188\times10^{-13}t^3 \quad \ldots (3)$$

From 300 to 650°C

$$a_t = 4{\cdot}0723+1{\cdot}1777\times10^{-4}(t-300)+1{\cdot}3049\times10^{-8}(t-300)^2 +1{\cdot}1384\times10^{-10}(t-300)^3 \quad \ldots (4)$$

Table 2. Coefficient of Linear Expansion α of Al

Temperature °C	$\alpha(°C^{-1})\times10^6$ a	b	c	Present work
0				23.0
50				23.8
100				24.8
150				25.7
200	26.2	31.2		26.7
250	27.0	31.6		27 7
300	27 9	32.0		28.6
350	28.9	32.5		29.5
400	30.0	33 0	29.9	30.4
450	31.0	33 4	30.6	31.7
500	32 1	33.9	31.4	33.4
550	33.5	34 3	32.2	35.5
600	35.4	34.8	34 1	38.1
650	37.2			41.0

(a) Simmons & Balluffi (1960a)
(b) Esser, Eilender & Bungardt (1938)
(c) Wilson (1942)

The coefficients of linear expansion defined by $\alpha = (1/a_t)(da_t/dt)$ are given in Tables 1 and 2 along with those determined by other workers. It is seen that our results agree reasonably well with those of other workers at lower temperatures but increase a little more rapidly at high temperatures.

It was found (as shown in figure 1 for Al) that the thermal expansion α increases considerably beyond a certain temperature ($\approx$ 350°C for Al and $\approx$ 550°C for Ag). It is assumed as in paper I that (i) eqs (1) and (3) hold up to the melting point, (ii) any deviations from them are due to the defects (figure 1) and (iii) the

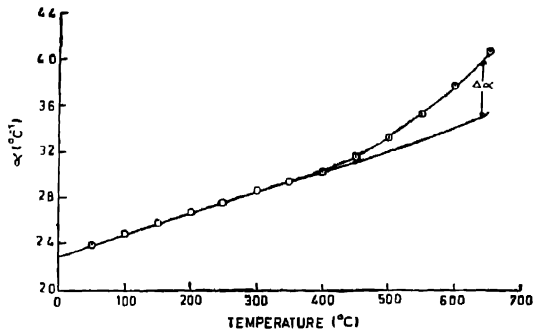

Fig. 1 Plot of coefficient of linear expansion of Al versus temperature.

energy of vacancy formation can be deduced from the slopes of the plots of log $\Delta\alpha$ versus $1/T$. Such plots are shown in figure 2. The energy of vacancy

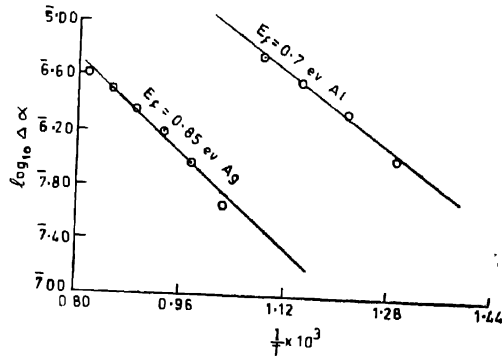

Fig. 2 Plot of logarithm of excess expansion versus reciprocal of temperature.

formation E_f determined from them are given in Table 3 and compared with the values of other workers.

Table 3. E_f values

Metal	E_f (eV) (from Fig. 2)	Other workers
Ag	0 85	1 01±0.03[a] 0.99±0 06[b] 0 93[c]
Al	0 70	0.71[d] 0.71[e] 0.65[f] 0 66[g] 0 67+0.03[h]

(a) Gertsrikon & Novikov (1960)
(b) Megervey & Triftshauser (1973)
(c) Yoshioki & Mori (1975)
(d) Bianchi et al (1966)
(e) Bass (1967)
(f) Seeger & Mehrer (1968)
(g) Mekoo et al (1972)
(h) Kim et al (1973)

Cartz (1955) has considered the temperature variation of thermal diffuse X-ray scattering and has shown that the amplitude of thermal vibrations of atoms in cubic crystals can be expressed in terms of the distance between neighbouring atomic positions and the melting point. He has shown that a "law of corresponding states" exists in the case of physical properties like thermal expansion which depend on atomic vibrations. The graph given by him between the reduced expansion $\alpha/\alpha_{m/2}$ and the reduced temperature T/Tm for cubic metals is a straight line in the range $0{\cdot}2 < T/Tm < \approx 0{\cdot}7$ and is given by

$$\frac{\alpha}{\alpha_{m/2}} = 0{\cdot}74+0{\cdot}52\left(\frac{T}{Tm}\right). \qquad (5)$$

Here Tm is the melting temperature and $\alpha_{m/2}$ is the thermal expansion at $T = \frac{1}{2}Tm$ The plot of $\alpha/\alpha_{m/2}$ versus T/Tm as obtained from our results is given in figure 3. It was found that the curve is linear only in the range $\approx 0{\cdot}1 \leqslant T/Tm \leqslant \approx 0{\cdot}45$ and is given by

$$\frac{\alpha}{\alpha_{m/2}} = 0{\cdot}75+0{\cdot}47\left(\frac{T}{Tm}\right). \qquad \ldots \quad (6)$$

Beyond about 0·45 (T/Tm) the curve deviates considerably from linearity although the points corresponding to the two metals silver and aluminium fall approximately on a common curve shown in full line.

Assuming that the law of corresponding states as given by equation (6) holds up to the melting point and that the deviation $\Delta(\alpha/\alpha_{m/2})$ from linearity is due to vacancies, it is possible to estimate the energy E_f of vacancy formation.

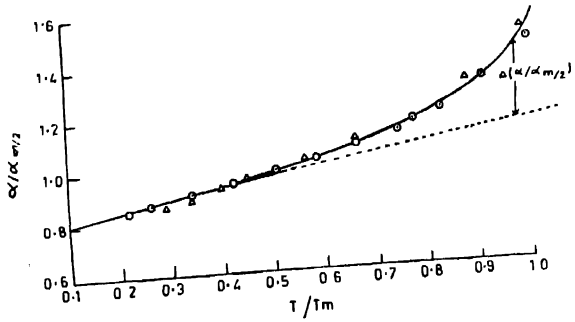

Fig 3 Plot of reduced expansion $\alpha/\alpha_{m/2}$ versus reduced temperature T/Tm. Tm is the melting temperature (°K) and $\alpha_{m/2}$ is the value of α at $T = \frac{1}{2}Tm$. Δ for *Al*, ⊙ for Ag.

Since thermally generated defects are randomly distributed in a crystal and since n/N, the defect concentration, is only of the order of 10^{-4} even at the melting point, we can expect a linear relationship $\Delta\alpha - Cn$ where C is a constant.

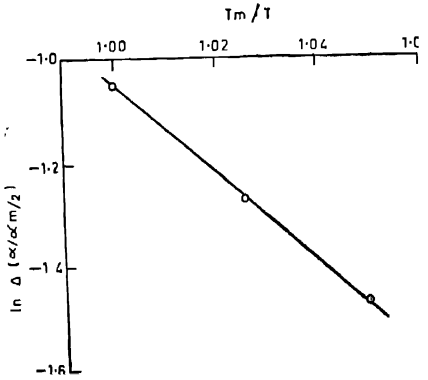

Fig. 4 Plot of excess reduced expansion versus reciprocal of reduced temperature.

Figure 4 shows the plot between the reduced quantities $\ln \Delta(\alpha/\alpha_{m/2})$ and Tm/T. This graph should be common to all the cubic metals. The slope of

Metal	Tm(K)	E_f (eV) observed	E_f (eV) equation (10)
Au	1336	0.98±0 02[a]	0 98
		0.94±0.99[b]	
		1 02±0.06[c]	
Ag	1234	1.01±0.03[d]	0.90
		0.99±0.07[e]	
		0.93[f]	
Al	933	0 71[g]	0 68
		0.71[h]	
		0.65[i]	
		0.66[j]	
		0.67±0 03[k]	
Cu	1356	1 14±0.06[l]	0 99
		1.05±0.05[m]	
		1.17±0.10[n]	
Pb	600	0.53[o]	0 44
		0.53±0.13[p]	
Pt	2042	1.40±0.10[q]	1 49
		1 30±0 10[r]	
		1.4[d]	
Mg	923	0 89±0.06[s]	0 67
Ni	1726	1.60±0.10[t]	1.26

(a) Flynn et al (1965) ; (b) Simmons & Balluffi (1972) ;
(c) Airoldi et al (1959) ; (d) Gertsrikon & Novikov (1960)
(e) Megervey & Triftshauser (1973) ; (f) Yoshioki & Moni (1975) ;
(g) Bianchi et al (1966) ; (h) Bass (1967) ;
(i) Seeger & Mehrer (1968) ; (j) Mckee et al (1972) ;
(k) Kim et al (1973 ; (l) Wrignt & Evans (1966) ;
(m) Johnson (1965, 1966) , (n) Simmons & Balluffi (1963) ;
(o) Feder & Nowick (1958) ; (p) Loadbotter et al (1966) ,
(q) Bradshaw & Pearson (1956) ; (r) Bacchella et al (1958) ;
(s) Beevers (1963) , (t) See text.

the line was found to be 8·47 and the intercept on the y-axis 7·42 so that we have

$$\ln \Delta \left(\frac{\alpha}{\alpha_{m/2}} \right) = 7{\cdot}42 - 8{\cdot}47 \left(\frac{Tm}{T} \right) \qquad \ldots \quad (7)$$

$$\ln \Delta\alpha = (7{\cdot}42 + \ln \alpha_{m/2}) - 8{\cdot}47 \left(\frac{Tm}{T} \right) \qquad \ldots \quad (8)$$

Thus the slope of the graph between $\ln \Delta\alpha$ and $1/T$ for any cubic metal should

be 8·47 Tm. Since under the present circumstances, $\Delta\alpha$ should be proportional to $\exp(-E_f/kT)$, we should have

$$8{\cdot}47\ Tm = \frac{E_f}{k}$$

or

$$E_f = 8{\cdot}47\ k\ Tm. \qquad \ldots\ (9)$$

If E_f is expressed in eV, we have

$$E_f(eV) = 7{\cdot}30 \times 10^{-4}\ Tm. \qquad \ldots\ (10)$$

The values of E_f calculated from eq (10) for various cubic metals are given in Table 4 and compared with the experimental values of other workers The value of E_f for nickel shown in column 3, Table 4, is not a measured value. It is calculated from the formula $E_f = 0\,55\,Q$, where Q is the activation energy for self diffusion The value of Q used for calculation is 66·8 K cal mole^{-1} given by Hoffman *et al* (1956). In view of the simple model used and the uncertainties in the experimental observations, the agreement is excellent.

6. Conclusion

Energies of vacancy formation in silver and aluminium have been estimated from the measurement of their thermal expansions at high temperatures. A relation between the energy of vacancy formation and the melting temperature is established and is found to be applicable to all cubic metals.

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